

Designing the Poly[1,5-bis(*N*-pyrrolyl)pentane as a New Horizon of Polypyrrole Paradigm with Its Structural and Optical Highlights

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Abstract

Poly[1,5-bis(*N*-pyrrolyl)pentane] (PBNPP) has been designed as a new addition to the modified polypyrrole family. This study entails the introduction of a pentane spacer between two pyrrole moieties and subsequently their oxidative polymerization under ambient conditions. The newly designed monomer and its polymer were fully characterized by FT-IR. The structural and optical behaviors were comparatively explored with reference to polypyrrole (Ppy), which was again prepared under same conditions. SEM was employed to visualize the morphology of PBNPP and Ppy comparatively. The data demonstrated the morphology of the PBNPP as spherical beads with a greater extent of surface porosity compared to Ppy, which possesses a compact granular form. The structural parameters were explored by XRD, where both possess crystallites of smaller size. Thermal behaviors were analyzed by TGA and DSC, where the newly designed polymer showed greater thermal stability and more plasticizing trend as compared to Ppy. Optical and HOMO-LUMO attributes have been characterized using UV-Vis. spectrophotometer and diffused reflectance spectroscopy (DRS). The PBNPP demonstrated greater molar absorption and lesser HOMO-LUMO gap as compared to Ppy. The PBNPP was proposed as a suitable candidate for photoconductivity compared with the Ppy. Thus, the polymer produced from the modified pyrrole

is thermally more stable, has high plasticizing character, reflects greater optically sensitivity and possesses ease of electronic transition compared to its counterpart.

Keywords: Poly[1,5-bis(*N*-pyrrolyl)pentane, Beads, HOMO-LUMO gap, Chains Separation, Thermal Resistance.

Introduction

The versatile character of Ppy has been the focus of a diverse range of research across the globe. It is known for its thermally viable [1], environmentally stable [2], biocompatible [3] properties as well as it being a reliable sensor [4]. It has been used as actuators [5], anticorrosive agents [6], enzyme immobilizers and in biomaterials [7]. Ppy has also been intensively studied as a nanocomposite material with reference to graphene [8], carbon nanotubes and other metal nanostructures [8]. It has been modified to improve its structural, mechanical, optical and electrical characteristics. These modifications of Ppy include C/N-alkylation [9,10], backbone functionalization, co-polymerization and metal chelation [11]. Ppy can be processed into thin films, powders, wires and tube-like structures dependent upon application. Every aspect of synthesis, modification and post processing proved beneficial to improve its structural, morphological and behavioral outcomes. Studies showed it to be a good electric and electronic material due to the highest conductivity and dielectric behavior [12,13]. Recent works with reference to Ppy are highly focused in application for smart plastics, flexible super capacitors, and electrode materials for Li Ions batteries [14,15].

The versatile nature of Ppy was further enriched by introducing an alkyl spacer between two pyrrole rings which linked their N-termini and converted them into *N*-functionalized bispyrrolyl moieties. Thus, a new modified form of pyrrole was synthesized and polymerized, in order to highlight the effects of this spacer introduction on the morphology, structure, thermal and optical behavior. It was further compared with pristine Ppy prepared and analyzed under identical conditions. The newly synthesized material demonstrated uniform bead-like globular structures, which could be excellently exploited for enzyme immobilization, catalytic support and as gas

sensor. It has further demonstrated the enhanced thermal resistance and plasticization character. Finally, its optical properties were investigated using UV-Vis and diffused reflectance spectroscopy, which showed its greater molar absorbance and smaller HOMO-LUMO gap. Thus, this newly synthesized polymer added new scientific data to the horizon of Ppy and paved the way for further exploring new modes of synthesis, functionalization and processing for different applications such as actuators, anticorrosive agents, electric and electronic materials.

Experimental

Materials

Pyrrole (BDH Chemicals, 99%, U.K), NaOH, FeCl₃ · 6H₂O (BDH Chemical LTD, U.K), NaH (Sigma Aldrich, Germany), 1-5 dibromopentane (Merk, 99.99%, Germany), Conc. HCl, Sodium Sulphate, THF (analytical solvent, Sigma Aldrich Germany), DMF (analytical solvent, Sigma Aldrich, Germany) n-Hexane (analytic solvent, Lab-Scan, Thailand) methanol (analytic solvent, Sigma Aldrich, Germany), ethanol (98%, Merk, Germany), acetone (analytical reagents, Sigma Aldrich, Germany), distilled H₂O.

Methods

Synthesis of poly[1,5-bis(*N*-pyrrolyl)pentane (PBNPP) was achieved by synthesizing 1,5-bis (*N*-pyrrolyl)pentane monomers and subsequently its polymerization. The method is described in two steps, as outlined below.

Synthesis of 1,5-Bis(*N*-pyrrolyl)pentane: 1.75 ml (0.01 molar) pyrrole was mixed in 4 ml tetrahydrofuran (THF), and added 0.06 M sodium hydride. It was kept in ice bath for half hour and added 1,5-dibromo pentane (0.005 M). The progress of reaction was monitored by thin layered chromatography (TLC). Reaction was completed within four hours and the reaction mixture was poured into cold water, neutralized and extracted in ethylacetate. The organic layer was further agitated using sodium sulfate (Na₂SO₄) as a dehydrating agent to completely remove the water. The product separated into the organic layer was concentrated under *vacuo*. The product was impurity free.

Synthesis of poly[1,5-bis(*N*-pyrrolyl)pentane] (PBNPP): The newly synthesized monomer 1,5-Bis(*N*-pyrrolyl)pentane was successfully polymerized in methanol using FeCl₃ as oxidizing agent. The obtained monomer “1,5-Bis(*N*-pyrrolyl)pentane” was mixed in 5 ml FeCl₃ solution by 1:4 molar ratio for further reaction. The reaction was allowed to proceed for 4 h. TLC was used to monitor the consumption of monomer for the growth of polymer. Finally, the product in form of black powder was filtered, and washed several times with distilled water to remove all impurities. It was dried overnight for further characterization.

Under similar conditions PPy has been prepared for comparative study.

Characterization

Formation of bispyrrolyl and its polymer was characterized by fourier transform infrared spectroscopy (FT-IR) (Affinity 1, MIRacle 10, Shimadzu Japan). Morphology of the synthesized PBNPP and PPy was characterized using SEM (FE-SEM TESCAN MIRA3MU, France). Structural information was obtained using X-Ray diffraction (XRD) data using a Bruker D-8 discoverer X-ray diffractometer manufactured in USA. The source of X-ray was Cu K α ($\lambda = 1.5408$ Å), and the tube voltage and current were 40 kV and 40 mA, respectively. Thermal resistance of polymer was analyzed by thermogravimetric analysis (TGA) using Q 50 V6.2 BUILD 187, TGA instrument and Tg was measured by DSC Q100 V8.2 BUILD 268, both manufactured in USA. Optical properties were measured under Shimadzu 1800, Japna, UV-Vis spectrophotometer. Band gap of as obtained polymer was analyzed by Perkin Elmer UV-Vis diffused reflectance spectrophotometer lambda 650 instrument, USA.

Results and Discussion

The synthesis of 1,5-bis (*N*-pyrrolyl)pentane and its polymer; poly[1,5-bis(*N*-pyrrolyl)pentane], designated as BNPP and PBNPP, respectively were characterized by FT-IR and their spectra were compared with that of pyrrole. There was a simple functional group conversion from cyclic amine to *N*-alkylated amine as shown in Scheme 1, where two pyrroles loss their H and linked with terminal C. The synthesized monomer “BNPP” was polymerized similar to pyrrole as reported elsewhere [16]. The FT-IR spectra of modified BNPP and PBNPP are shown in Figure 1 (A and B). According to Figure 1A, the disappearance of a band in the region from 3500 to 3100 cm⁻¹

and an appearance of a band at 2926 cm^{-1} are indicating the replacement of an N-H bond by an N- $\text{C}_{(\text{aliphatic})}$ bond [17, 18]. The stretching vibrations appearing at 2926 cm^{-1} band indicate the CH_2 attributed to the incorporation of the *n*-pentane spacer [19]. The band at 2850 cm^{-1} is due to the C-H from the pyrrole ring. The absorption band at 1319 cm^{-1} is due to C-N stretching. The absorption at 1630 cm^{-1} is characteristic of pyrrole ring vibrations [20]. These IR bands confirm the synthesis of 1,5-bis[(*N*-pyrrolyl)pentane] had been successful. The ring and chain bending out of plane are reflected at 775 cm^{-1} and 721 cm^{-1} , respectively [21]. It further confirmed the presence of pentane spacer in pyrrole moieties. The FT-IR spectrum obtained supported the theory that the conversion of pyrrole into BNPP had been successful.

Similarly, Figure 1 B shows the FT-IR spectra for the PBNPP, where all corresponding bands are much broader. The aromatic pyrrole and aliphatic pentane bands were present at 2840 cm^{-1} and 2910 cm^{-1} (respectively), which are almost identical to those observed in Figure 1A. The aromatic ring symmetric and anti-symmetric stretching appeared at 1650 cm^{-1} and 1540 cm^{-1} respectively together with a shoulder band spreading from $1340\text{--}1440\text{ cm}^{-1}$ which is due to N-C stretching. The CH deformations appeared in the range of 1000 cm^{-1} to 1100 cm^{-1} . The broader band at 900 cm^{-1} is due to the out of plane bending of the aromatic ring due to varying number of repeat units in as produced chain length. Finally, the band observed at 780 cm^{-1} is the characteristic for the polymerization of the pyrrole as reported elsewhere [16, 22].

The morphology of the polymer was compared in Figure 2 A&B. Figure 2A shows the morphology of Ppy, which is exactly as reported by N. G Sahoo *etal* and M. Omastava [23,24] where Ppy was synthesized under the same conditions. Figure 2B shows the morphology of then PBNPP, prepared under identical conditions. There is a notable change in the morphology of the polymer when converted into PBNPP from Ppy. The introducing of the *n*-pentane spacer produced well defined globular form with minimal appearance of the Ppy like granules. It has also possessed small pores which may make it an important material for adsorption, storing and sensing of different gases like NH_3 , CO and NO_2 [22,25,24]. It may also hold potential in the clinical detection of uric acid, urea and glucose etc. in comparison with Ppy that have been applied for such applications [27]. The as globular structure observed may also possess greater plasticizing behavior which could be used for further modification to make a highly refined membrane for selective exchange.

The structural change produced in converting the Ppy into PBNPP was analyzed using XRD and the data is shown in Figure 3. The material which was produced under identical conditions is amorphous, but possesses crystallite of different sizes. Herein, average chain separation is calculated using Equation 1 [28].

$$S=5\lambda/8\sin \theta \quad (1)$$

According to Equation 1, S is the average chain separation, λ is the X-ray wavelength, θ is the diffraction angle at the maximum intensity in the graph. The average chain separation of PBNPP and Ppy is found as 2.30 nm and 2.49 nm respectively. Similarly, average crystallite size in the amorphous polymer was found through the Scherrer formula given in Equation 2 [29].

$$D=K \lambda / \beta \cos \theta \quad (2)$$

Where D is crystallite size, θ is the diffraction angle at maximum peak intensity, β is the full width with half maximum in radians, and k is the shape factor with value of 0.89. The average crystallite sizes were deduced for PBNPP and Ppy as 8.4 nm and 14 nm respectively. These values demonstrated that a greater extent of amorphous character was present in the PBNPP as compared to the Ppy. The XRD data supported this notion that the globular morphology is more amorphous as it has been seen in many bead forms of polymer [30].

Thermal stability analysis of the PBNPP from the modified pyrrole monomer is shown in Figure 4 and is compared with the reported data achieved under identical conditions. The sample was heated from 20 °C to 650 °C at the rate of 5 °C/minute. According to Figure 4, the polymer weight loss occurred between 260 °C - 600 °C, was not sharp. It can be postulated that there may be some polymer chains in granular form on the surface of the globular structure, and hence these would be degraded first. Furthermore, varying chain lengths also produce similar thermograph. According to the study of C. Cassagnol and N. G Sahoo, pure Ppy synthesized under similar conditions showed weight loss at 180 °C with no stability in any region observed before complete degradation [23,31]. Similar results have also been shown elsewhere [22]. The improvement of thermal resistance is attributed to the crosslinking factor, which is expressed in Scheme 2. The crosslinking factor might have developed aromatic π - π stacking to some pyrrole units and hence increased their thermal stability. Therefore, formation of different chain lengths, granular to globular morphology and π - π stacking effect limited to some pyrrole units has enhanced significant

thermal stability which only has been achieved when Ppy modified into PBNPP by introducing the pentane spacer.

The effect of plasticizing temperature on change of morphology of Ppy from granular to globular in PBNPP was investigated using differential scanning calorimetry (DSC) noting their Tg values. The values are recorded at the similar rate give in TGA analysis, i.e 5°C/minute. The comparative data in plot form is given in Figure 5. Ppy demonstrated its plasticizing temperature at 135 °C, which is in accordance, based on morphology to many published data as [16]. The, Ppy analogue PBNPP, produced a globular morphology, which is less tightly packed and possesses greater voids. Therefore, it showed greater plasticizing behavior by demonstrating a reduced Tg value *i.e.* at 117 °C. This may be further reduced for absolute globular structures and for larger globules. Therefore, study is still open for further exploration to relate plasticizing effect by producing new globular size.

The optical behavior of PBNPP was compared with Ppy, the data is shown in Figure 6A and 6B, respectively. PBNPP and Ppy were dispersed in reagent grade ethanol using a sonicator. The stable dispersion was analyzed under UV-Vis spectrophotometer. The dominant shoulder in case of Ppy is reflected at 400 nm, which is purely benzenoid behavior [32]. PBNPP possessed a λ_{\max} at 500 nm, which is quite red shifted. The modification of Ppy into PBNPP did not changed the benzenoid configuration, but the red shifting depicts that the pyrrole rings in the PBNPP may have developed π - π stacking resulting in the decreased excitation energy.

The electronic transitions and band gap *i.e.* Eg is measured using differential reflectance spectroscopy (DRS) and is shown in Figure 7. The values for Ppy and PBNPP appeared at 643 nm and 654 nm respectively. According to Equation 3, given below, these can converted to electron volts (eV) [28].

$$E_g = 1240 / \lambda_{\text{excitation}} \quad (3)$$

The calculations showed the band gap of Ppy and PBNPP is 1.9 eV and 1.8 eV respectively. Therefore, the newly synthesized polymer is expected to be suitable for use as a semiconducting material.

Conclusions

Modification of pyrrole into 1,5-bis(*N*-pyrrolyl)pentane resulted in a desirable molecule possessing a preferable morphological appearance in the polymeric form. Such transformation lead to the production of globular form rather than granular. The globular microstructure revealed porosity which ensures high potential for the anchoring of catalysts, enzymes or other biomolecules of interest. Additionally, it showed improved thermal resistance and plasticizing character as compared to Ppy, which guaranteed the durability. It demonstrated increased optical molar absorption and decreased the band gap for electronic transitions as characterized by UV-visible and DRS. This property is essential for making it suitable candidate for photo-electric devices. It possessed reasonable crystallite size which predicated the crystalline transformation by optimizing polymerization conditions. The PBNPP is a new polymer that is widening the application of polypyrroles across multiple sectors. Further studies focusing on application specific uses will elucidate the full potential of this exciting polymer.

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Compliance with Ethical Standards

Conflict of Interest: The authors disclose that they have no conflict of interest.

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Figure 1. FT-IR spectra of BNPP and PBNPP are given as A and B, respectively.

Figure 2. SEM micrographs of Ppy (A) and PBNPP (B) synthesized using FeCl_3 as an oxidizing agent under identical conditions.

Figure 3. XRD pattern of Ppy and PBNPP, respectively.

Figure 4. Thermal degradation of PBNPP synthesized using FeCl_3 .

Figure 5. DSC curves of Ppy and PBNPP synthesized under identical conditions.

Figure 6. UV-Vis absorptions of A: PBNPP, B: Ppy, respectively.

Figure 7. DRS behavior and Kubelka Munk Interpretation of PBNPP and its comparison with Ppy is given, respectively.

Scheme 1. Conversion of pyrrole into bis-pyrrolyl pentane.

Scheme 2. Structure of PBNPP and its crosslinking pattern.